

Radio-Frequency Power Graded Hydrogenated Amorphous Carbon Films on Diverse Substrates

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Abstract—Diamond-like carbon (DLC) films are increasingly used for optical and biological components. Yet the stability of the film, including adhesion and duration are still to be developed. Hydrogenated DLC films (hydrogenated amorphous carbon, a-C:H) were deposited onto transparent substrates by applying a graded radio-frequency (RF) power by plasma-enhanced chemical vapor deposition (PECVD). The a-C:H film, formed by constant RF power was synthesized for comparison. Raman spectra, X-ray photoelectron spectra (XPS), field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM) were used to characterize the film structure along with surface morphology and roughness on the diverse substrates. Tribological properties and adhesion were obtained by friction-wear experiment and scratch tests. Light transmittance was determined by UV/Vis spectra. The results have revealed that films deposited on the various substrates had typical diamond-like features and there were obvious residual stress relaxation and better adhesion for the graded a-C:H films.

Keywords—a-C:H; Microstructure; Residual stress; Adhesion; AFM

I. INTRODUCTION

Diamond-like carbon (DLC) films have many attractive mechanical and optical properties. Researches towards industrial applications of DLC films were widely carried out in the past decades and remarkable successes have been achieved. Protective layers on engineering tools and hard storage discs are the primary uses as a result of its extreme high hardness and wear-resistance [1-2]. DLC films also can be the antireflective coatings for IR optics due to the transparency in the Vis and IR range [3]. Generally, thick films are required to provide protection. However it was reported that DLC films peeled off from the underlying substrates were with thicknesses exceeding 1 μm or even 200 nm [4-5]. High residual stress in the DLC films is mostly responsible for this observed poor adhesion. Successive energetic ion bombardment to the growing film surface during the deposition process leads to intrinsic compressive stress in the unbalanced film structure, which is the dominating part of the residual stress [4]. Thus high sp^3 bond content usually accompanies with large intrinsic compressive stress. The tribological property of DLC films are greatly influenced due to the residual stress, with the film continuity and durability being deteriorated. There would be thickness limitation to guarantee enough adhesion of the films coated on substrates. A series of ways were adopted to reduce residual stresses on the films. Addition of interlayers is a common method to reduce such stress. Chehung Wei et al. used two interlayers of chromium and titanium to improve adhesion [6]. Certain elements or metal particles are doped to obtain DLC films of low residual stress, such as Si, N, Ti, Cu and Al [7-11]. Besides, annealing treatment and gradient films are also effective methods [12-14].

Hydrogenated DLC films, i.e. hydrogenated amorphous carbon (a-C:H) are relatively soft and polymeric. In this study, a-C:H films are prepared using plasma enhanced chemical vapor deposition (PECVD) with graded RF power on several transparent substrates which tend to be used in the optical and biological fields, such as glass, indium tin oxide (ITO) coated glass and polyethylene terephthalate (PET) substrates.

II. EXPERIMENTAL

A. Deposition of the a-C:H Films

The a-C:H films were prepared by a self-made PECVD device shown in Fig.1, with a magnetic filed adopted on the cathode plate to control the plasma trace. Prior to deposition, the substrates were cut into 25mm \times 25mm. The ITO (1.1mm thickness, 10 Ω) glass and PET substrates were cleaned in acetone and absolute alcohol each for 15minutes. Silica glass and frosted glass substrates were bathed in alkali solution and acid solution each for 3 hours, with acetone and absolute alcohol cleaning ultrasonically both for 15 minutes succeeded. All the substrates were dried by nitrogen and placed on the anode plate. The distance between the cathode and anode plates was 100 mm. The base pressure in the vacuum chamber was 7.5×10^{-3} Pa. C_4H_{10} and Ar were employed as the reaction gas and the flow rate was 1.5:25. Pre-treatment of Ar^+ bombardment was taken for 15 minutes. During the deposition process, the RF power was stepwise increased from 510 W to finally 720 W for altogether 40 minutes. Therefore, the film composition (sp^3/sp^2 ratio) would be graded through the whole film. The single a-C:H film was deposited on silica glass with constant RF power of 720 W at the same time.

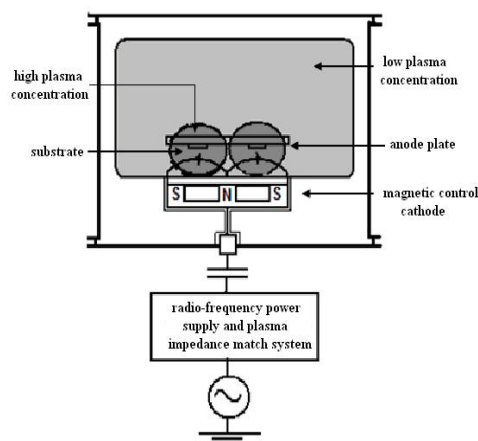


Fig.1. Schematic diagram of radio-frequency magnetron PECVD deposition device

B. Characterization of the a-C: H Films

The type of bonds, relative content and evaluation of residual stress were analyzed by visible Raman spectroscopy of LabRAM HR, with the laser excitation at the wavelength of 532.1nm. The film composition was measured by X-ray photoelectron spectroscopy of PHI5300. Surface morphology and roughness were characterized by AFM spectroscopy of Dimension Icon in scanAsyst mode. MS-T3000 friction-wear spectrometer was used to obtain the wear curve and friction coefficient in the ambient environment. The stainless steel ball was used as the counterpart and its rotation speed was 100 rev/min. The load applied was 200 mN. Scratch test was carried out to examine the adhesion strength by WS-2004 scratch tester, with the indenter running speed of 4 mm/min and maximum load of 100N. The morphology of the scratch fragment was seen by field emission scanning electron microscopy of HITACHI SU70. The light transmittance was obtained by ultraviolet-visible (UV-vis) spectrophotometer of TU-1901.

III. RESULTS AND DISCUSSION

A. Bonding Microstructure and Surface Morphology

Bonding structural characteristics of DLC films are generally given by Raman spectroscopy. The typical Raman spectrum of DLC films is a broad band between 1200 cm^{-1} and 1800 cm^{-1} which is centered near 1560 cm^{-1} and can be deconvoluted into D peak and G peak by Gaussian fitting. The D band arises from the breathing vibrations of the six-fold aromatic rings of A_{1g} mode at about 1350 cm^{-1} . The G band is due to the stretching vibration mode of sp^2 sites both in rings and chains at about 1580 cm^{-1} . The Raman signal of sp^2 sites is more than 50 times stronger than that of sp^3 bonds, so Raman spectrum of the film is actually dominated by sp^2 sites without direct sp^3 bonding information. Specific details of sp^3 and sp^2 bonds can be provided by the Gaussian fitting parameters of peak position, intensity ratio of I_D/I_G and FWHM of the two fitting peaks. Usually, various deposition conditions can cause the peak shift. Both bond angle removal and bond length disorder lead to a downward shift of the G peak position [15-17].

Raman spectra of the graded and single a-C: H films on different substrates are shown in Fig. 2. It is observed that the Raman spectra of the A-C: H films have similar shapes of the broad asymmetric peaks. The D peaks at about 1350 cm^{-1} and G peaks at around 1590 cm^{-1} are seen exhibiting typical Raman features of DLC films (Fig. 1b). The Gaussian parameter of I_D/I_G ratio often correlates with the sp^2 and sp^3 bonds content. Lower I_D/I_G ratio with the downward shift of G peak position is corresponded to higher sp^3 bonding fraction [18]. It is indicated from the fitting parameters summarized in Tab. 1 that there is minimum sp^3 content for the graded a-C: H film on PET substrate according to its biggest I_D/I_G ratio, which is probably caused by the organic composition of the substrate beneficial for the stable sp^2 configurations. Nevertheless, the Raman fitting information is easily influenced by slight bonding changes of a-C: H films. Though I_D/I_G of the graded a-C: H film on ITO substrate is smaller than others, its G position shifts upward relative to the single film. A positive correlation exists between FWHM of G peak and sp^3 content [19]. sp^3 content increases when the G peak is in a lower position with larger FWHM. Consequently, it can be concluded that the single film gets the maximum sp^3 content due to its maximal FWHM of G peak comparing with

the graded films on diverse substrates. The reasonable explanation is that constant energetic ions impacted to the film by higher RF power easily bring in residual stress concentration which tends to induce more sp^3 sites than the graded RF power. J. Schwan et al. has proved that FWHM of the G peak was linearly corresponding to the inner stress of DLC films [19]. Decrease of the residual stress would result in a reduction of the FWHM. Therefore, the residual stress can be predicted to decrease by using the graded RF power. Additionally, there is particularly less stress concentration for a-C: H on PET than on other substrates (Tab. 1). FWHM broadening of G peak also reflects the disorder of bond angle and bond length as well as decrease of the sp^2 cluster size [16]. As thus it's suggested that the bonding structure of single a-C: H is more disordered than that of the graded a-C: H films.

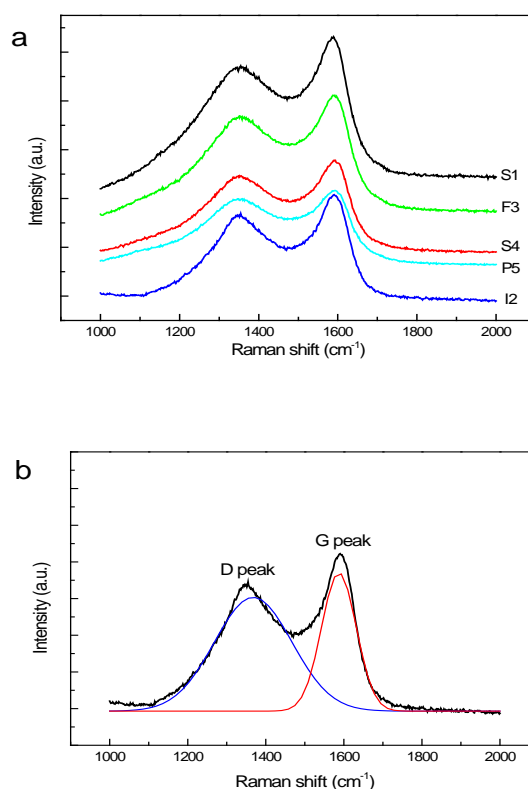


Fig.2. (a) Raman spectra of the a-C: H films on diverse substrates (b) Gaussian fitting peaks of the graded a-C: H on ITO glass substrate

TABLE 1
GAUSSIAN FITTING PARAMETERS OF THE A-C: H FILMS

NO.	Substrate	Power type	D peak position (cm^{-1})	G peak		I_D/I_G
				Position (cm^{-1})	FWHM (cm^{-1})	
S1	SiO ₂ glass	Single power	1354.69	1589.06	92.55	2.35
I2	ITO glass	Graded power	1354.69	1590.63	89.10	1.84
F3	Frosted glass		1353.13	1592.19	89.78	2.40
S4	SiO ₂ glass		1351.56	1593.75	87.49	2.58
P5	PET		1348	1593.75	85.29	3.10

The XPS spectrum of the graded a-C: H film on ITO substrate is shown in Fig. 3. Next to the C1s band at 284.58 eV, O1s band at 551.20 eV is observed. (Fig. 3a). The C 1s peak is fitted by three peaks representing C sp^3 at the binding energy of 284.89eV, C sp^2 at 283.31eV, and C=O at 287.69eV (Fig. 3b). sp^3 bonding fraction is directly measured by the ratio of sp^3 peak area over the whole C 1s peak area [20].

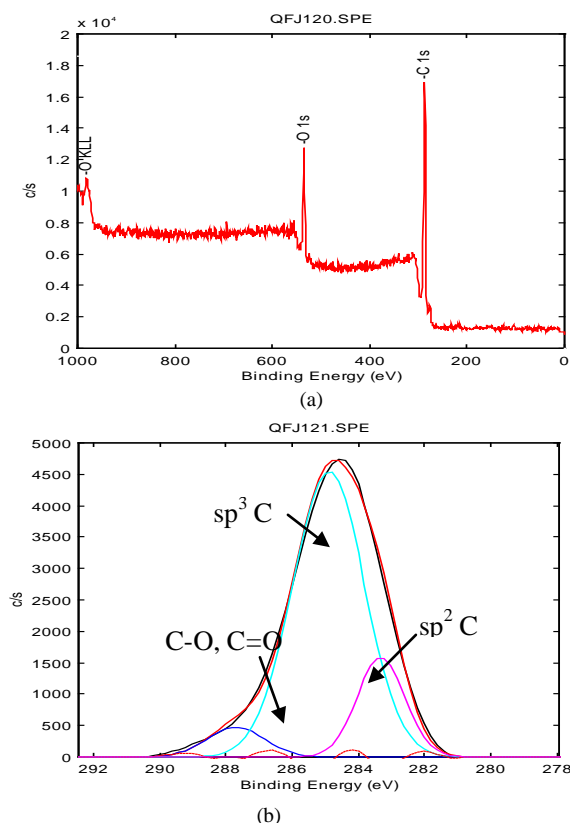


Fig.3. (a) XPS spectrum of the graded a-C: H on ITO glass substrate and (b) XPS spectrum of the C1s peak

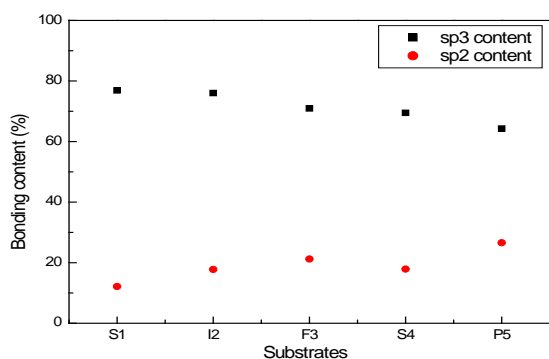


Fig.4. Bonds content of the films obtained by XPS spectra

Fig. 4 shows the bonding fraction of the a-C: H films. As can be seen, surface sp^3 fraction of the graded films is lower than that of the single a-C: H which is up to 76.90%. However, sp^2 fraction is decreased for the graded films. The a-C: H on PET substrate especially exhibits the lowest sp^3 bonding content which corresponds with the Raman analysis. (Fig. 2a). Therefore the graded manner of RF power not only helps forming the structure that sp^3/sp^2 ratio stepwise distributed throughout the film, but also bring in the surface sp^3 fraction reduction, as a result of which the film residual stress can be

lowered and the film continuity reinforced. But sp^3 fraction of the graded a-C: H films still keeps in high values so as to provide enough protection once coated on certain biological or optical components.

Fig.5. displays the AFM images of the a-C: H coating on different substrates. It is clearly shown that segregation of the carbon particles happened in partial areas of the single a-C: H, thereby the film continuity and smoothness would be influenced. In contrast, the graded a-C: H films are uniformly distributed on the substrates. The difference is that individual spherical particles compact on silica glass substrate to form the graded a-C: H but it appears in a lamellar structure on ITO glass substrate while flocculently positions on PET substrate. Due to the rough appearance of the frosted glass, the image of the a-C: H on it can't be clearly given.

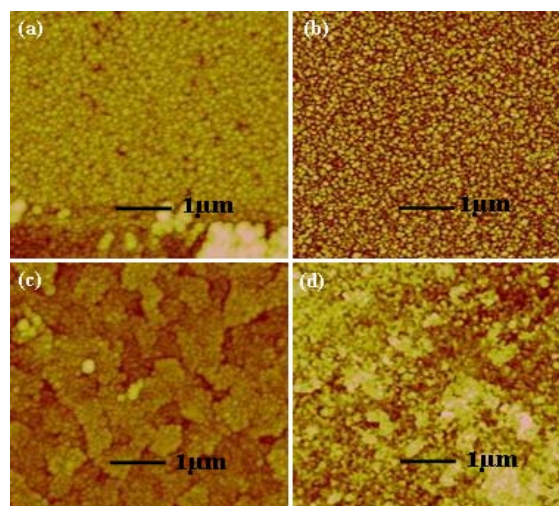


Fig5. AFM images of the films (a) single a-C: H (b) graded a-C: H on SiO₂ glass substrate (c) graded a-C: H on ITO glass substrate and (d) graded a-C: H on PET substrate.

The average roughness of the a-C: H is illustrated in Fig.6. Obvious decrease of roughness can be observed for the graded a-C: H films. The a-C: H on the frosted glass substrate owns the lowest roughness primarily attributed to the coarse surface appearance in favour of deposition of the fine carbon particles and prevention against carbon segregation. Consequently it's indicated that the graded RF power would avoid excess carbon molecules from decomposing and deposition so to generate the irregular and aggregated surface, and the morphology of the graded films differed from each other according to the substrates on which they are coated.

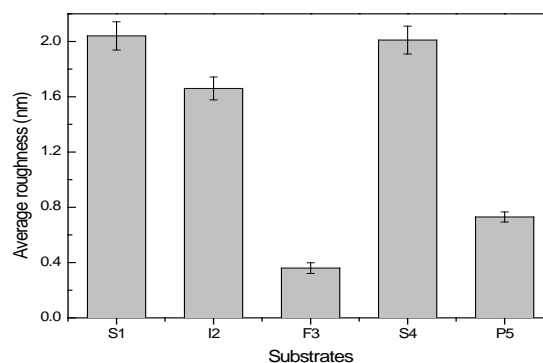


Fig.6. Average roughness of the a-C: H films on different substrates

B. Tribology and Adhesion

Fig.7. presents the wear curves of the a-C: H films. There are obvious increases of the friction coefficient above 0.1 at the beginning for the films and then fall back to 0.1 below as the rotation goes on. In compare with the single a-C: H, wear curves of the graded films work smoothly on the whole. The friction coefficients of graded films coated on silica glass, ITO glass and the frosted glass substrates are approximate when the wear curves operate in the steady state, and the value is particularly in a low level for a-C: H on PET substrate than others. Besides, it's noticed that the wear curve of the single a-C: H tends to rise at the end of the test while it is on the contrary for the graded films.

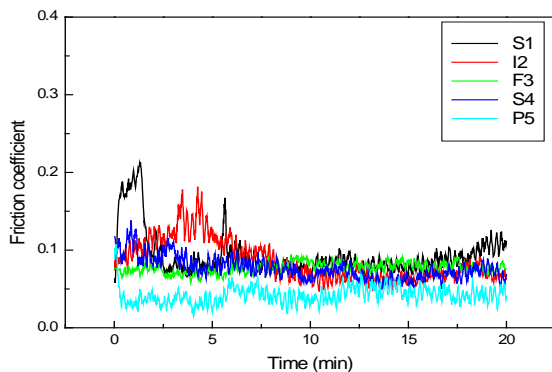


Fig. 7 Variation of friction coefficient against time

With the observation mentioned above, it's merited that the largest average friction coefficient of 0.093 belongs to the single a-C: H, nevertheless the graded a-C: H on PET substrate has the smallest friction coefficient of 0.042 shown in Fig.8. The friction coefficient of graded films on the three types of glass substrates is generally around 0.08. The hydrogen in the a-C: H film can eliminate the free σ -bonds on the film surface which is the main reason for the low friction coefficients [21]. Graphitization of the wear debris lubricates the friction surface that reflects the smooth wear curves. Because the graded structure of a-C: H has lowered the residual stress and promoted the film durability, the friction coefficient of graded a-C: H films is rather low. The surface condition of substrate will also affect the tribological property of a-C: H films.

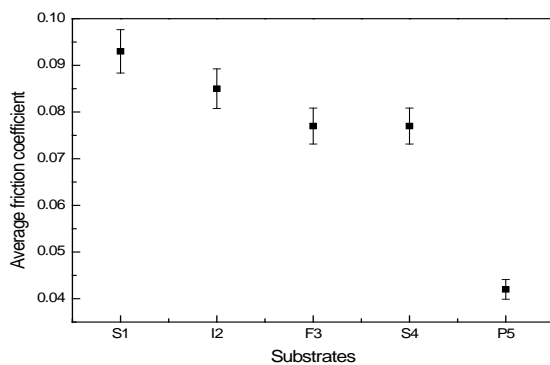


Fig.8 The average friction coefficient versus the substrates

Results of the scratch test are shown in Fig.9. The critical load where the acoustic signal begins to change sharply in the

curves with the film adhesive failure can act as a measurement of the film-substrate adhesion strength. The critical load of the single a-C: H is 94.65N. However, it's far beyond the maximum load of 100N for the graded a-C: H on PET and silica glass substrates. The critical load of a-C: H on the frosted glass substrate is still over 100N which will not be affected by the fluctuation of the scratch curve owing to the rough surface of the substrate itself. Only the a-C: H on ITO substrate has the critical load of 94.475N close to that of the single a-C: H. Thus it confirms the improved and more sufficient adherence of the graded a-C: H on the transparent substrates. In addition, the residual stress of the graded a-C: H is indicated to be markedly reduced by comparing the scratch curves.

Fig. 10 is the FESEM image of the graded a-C: H film fragments around the scratch trace on silica substrate. It is obvious that the a-C: H peels off from substrate in the shape of flakes.

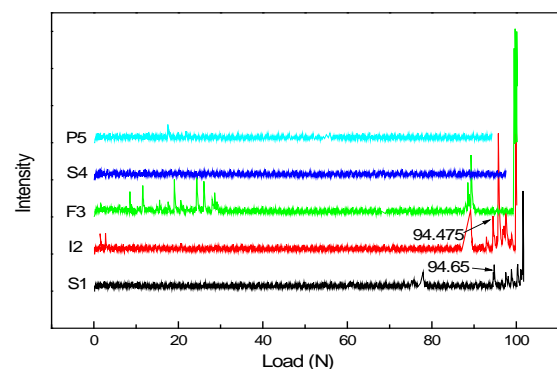


Fig.9 Scratch curves of the a-C: H films.

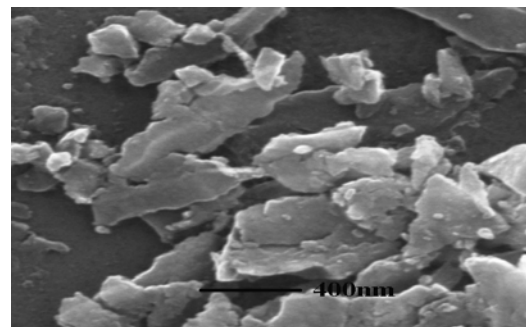


Fig.10 SEM morphology of the a-C: H film fragments

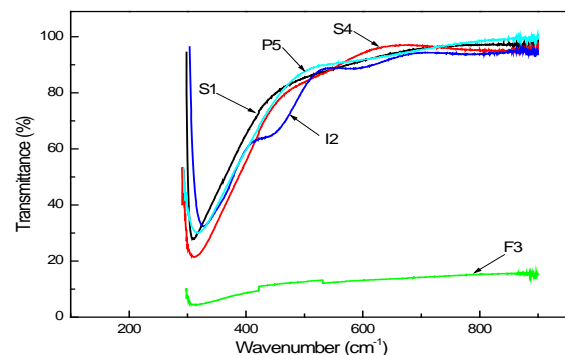


Fig.11 UV/Vis spectra of the a-C: H films.

C. Optical Property

UV/Vis spectra of the a-C: H films are presented in Fig. 11. The single and graded a-C: H films on PET and silica glass substrates have similar light transmittance curves.

There is a stepwise rise of the light transmittance between the wavelength 300 nm to 700 nm for the a-C: H coated on ITO substrate probably related to multilayer of indium tin oxide film and the a-C: H film. The light transmittance of a-C: H on the frosted glass substrate caused by its irregular surface condition is less than 20%, while it is the highest beyond 700 nm for a-C: H on PET substrate. The light transmittance of a-C: H films on silica glass, ITO glass and PET substrates is all greater than 90%, exhibiting excellent transparency of the a-C: H in the visible and near-infrared light region.

IV. CONCLUSIONS

The gradient A-C: H film structure of relatively more sp^2 sites at the film-substrate interface and higher surface sp^3 bond content help ease the severe ion bombardment to the growing film during the deposition process. So the residual stress of the graded a-C: H will be greatly reduced compared with the a-C: H prepared by constant RF power which gets the confirmation from Raman spectra analysis and scratch tests. Moreover, surface quality of the graded a-C: H is improved given by the AFM images. Therefore, the graded a-C: H provides good tribological property of stable wear curve and lower friction coefficient. Film on PET substrate particularly shows favorable adhesion as well as frictional and optical property. In conclusion, the graded a-C: H we synthesized is a proper candidate for the protective coatings on biological and optical substrates.

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